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## TYPES AND COMPOSITIONS OF CRYSTALLINE GLAZES (A Review)

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The data on synthesis and research of various crystalline glazes published in the literature are summarized. The types and compositions of glazes, as well as their structural specifics, firing conditions, and areas of application are described. The effect of the phase composition on the decorative properties of crystalline glazes is shown.

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Devitrification or crystallization of glazes is undesirable in industrial production. However, what is known as crystalline glazes are at present widely used to improve the decorative properties of ceramic products.

Articles with crystalline glazes first appeared in 960 – 1279 during the Song dynasty in China. Crystalline glazes are crystallized glasses which are used for coating of artistic, household, sanitary, or construction ceramic products. The demand for crystalline glazes increased substantially over the last few years due to the special interest shown by the designers of ceramic articles.

In special firing conditions, crystalline glazes release numerous crystals of different sizes and colors. According to the size of the crystals, the glazes are divided into macrocrystalline and microcrystalline ones. The former contain crystals whose size can attain several centimeters, and the latter are nontransparent, opacified, and contain fine crystals invisible to the naked eye.

According to the type of released crystals, the glazes are distinguished as hematite, anorthite, pyroxene, titanium, zirconium, aventurine, manganese etc. [1, 3]. Table 1 gives the typical compositions of crystalline glazes.

**Hematite crystalline glazes** represent one of the most ancient types of macrocrystalline glazes [3]. They were already known in the early 12th century. Articles (tableware, vases) coated with these glazes were specially made for the Emperor's court.

As hematite glazes are fired, agglomerations of their principal crystalline phase, i.e., crystals of  $\alpha\text{-Fe}_2\text{O}_3$  hematite, are formed against the background of yellow or brownish-black glaze glass [5]. These glazes can be deposited on both porcelain and faience products. Their maximum firing tem-

perature is 1300 – 1350°C. The chemical composition of hematite crystalline glazes is as follows: (wt.%): 60 – 70  $\text{SiO}_2$ , 12 – 20  $\text{Al}_2\text{O}_3$ , 5 – 8  $\text{Fe}_2\text{O}_3$ , 5 – 10  $\text{CaO}$ , less than 5 ( $\text{K}_2\text{O} + \text{Na}_2\text{O}$ ), less than 3  $\text{MgO}$ , slight quantities of  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$  etc.

The grain type and sizes and the relative quantities of released crystals vary depending on the glass composition, firing conditions, and the nature of the furnace gas medium. The gas atmosphere in the firing furnace has a strong effect on the type of the released crystalline phase in iron-bearing glazes [4]. Thus, hematite  $\alpha\text{-Fe}_2\text{O}_3$  crystals are formed in glazes in oxidizing conditions, and magnetite crystals  $\text{Fe}_3\text{O}_4$  are formed in reducing conditions. Moreover, due to the high content of  $\text{Al}_2\text{O}_3$  (12 – 20%) and  $\text{CaO}$  (5 – 10%), anorthite crystals  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  are also identified in hematite glazes.

Chen Xianqui with co-authors [14], using the electron microscope and the electron microprobe, identified the structure of hematite glazes. According to their data, the glass structure is formed as a result of the double phase separation of the glaze glass. In the primary phase separation, small drops enriched with iron are formed, which later enlarge or aggregate to become a continuous phase. After the secondary phase separation in an oxidizing medium, hematite crystals emerge whose agglomerates form a red or a brown pattern, and the iron-deficient phase is formed.

**Anorthite crystalline glazes** also have a long history (approximately since the middle of the 13th century) [1]. These glazes contain a great amount of anorthite crystals  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  which are uniformly and with high dispersion distributed over the entire glaze layer in the form of fine needles below 1  $\mu\text{m}$  in size. Therefore, these glazes are attributed to the microcrystalline group. The degree of

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opacification of anorthite glazes depends on the amount of emerging anorthite crystals.

The glaze composition is highly calciferous; it belongs to the  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system and is usually located in the primary crystallization field of anorthite or near the boundary line between the primary crystallization fields on anorthite and tridymite: 65–70%  $\text{SiO}_2$ , 16–18%  $\text{Al}_2\text{O}_3$ , 10–14%  $\text{CaO}$ , whereas  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$  and other oxides are contained in relatively slight quantities. Under certain firing conditions, anorthite easily crystallizes in these glazes. Moreover,  $\text{Fe}_2\text{O}_3$  (about 2%) is often contained in the glaze composition as a coloring agent. When the glazes are fired in a reducing medium, the  $\text{Fe}^{3+}$  ion passes to a lower oxidation degree, which imparts a green color to the glazes. Depending on the concentration of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions, the color of the glazes varies from yellowish-brown to green [6]. Apart from  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{CoO}$ , and  $\text{MnO}_2$  can be introduced as well to the composition of anorthite glazes in the capacity of coloring agents.

**Pyroxene crystalline glazes** belong to the macro-crystalline group [3]. Their main crystalline phase is repre-

sented by pyroxenes which are compound minerals with the common chemical formula:  $XY\{\text{Si}_2\text{O}_6\}$  ( $X$  are eight-coordination cations:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ;  $Y$  are six-coordination cations:  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ;  $\text{Si}$  is in four coordination [ $\text{SiO}_4$ ]).

Pyroxene crystals of different compositions often acquire various shades due to their specific structure. For example, bronzite has green, brown, or bronze color; hypersthene varies from dark green to black, which is responsible for the high decorative effect of these glazes.

The chemical composition of pyroxene glazes can be classified as the  $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system with 5–10%  $\text{Fe}_2\text{O}_3$  additive or without it. The Seger formula for these glazes can be represented in the following way:

$$0.10(\text{K}_2\text{O} + \text{Na}_2\text{O}) \cdot 0.38\text{MgO} \cdot 0.52\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot y\text{SiO}_2.$$

The firing temperature interval for these glazes is 1270–1310°C, and the gas medium in the furnace does not have a substantial effect on their production.

TABLE 1

Glazes	Mass content												Firing temperature, °C	Reference
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	ZnO	BaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>		
Hematite	60.92	19.08	6.78	2.03	2.70	0.10	–	–	6.50	0.62	–	1.27	1300 – 1350	[4]
	61.88	18.05	7.47	2.10	3.22	0.10	–	–	5.45	0.39	–	1.34	1300 – 1350	[5]
Anorthite	67.20	14.31	10.02	0.58	4.19	0.14	–	–	1.20	0.07	–	0.19	1300 – 1350	[6]
	68.95	13.92	8.67	0.66	4.42	0.14	–	–	0.89	0.02	–	0.18	1300 – 1350	[6]
Pyroxene	62.30	12.90	10.30	2.01	2.90	1.00	–	–	6.90	0.70	–	0.30	1270 – 1320	[7]
	57.80	14.80	17.10	2.60	1.70	0.80	–	–	3.20	0.70	–	1.00	1270 – 1320	[7]
Willemite	48.43	0.98	6.12	0.66	6.60	5.44	23.20	0.23	0.08	–	8.40	–	1150 – 1200	[1]
	46.89	0.81	7.02	0.36	7.63	4.77	22.31	–	0.04	–	9.90	0.24 CoO	1150 – 1200	[1]
	49.42	5.17	4.05	1.94	1.33	7.48	25.56	0.11	0.32	–	3.08 MnO	0.02	1200 – 1280	[1]
	55.17	3.79	3.98	2.56	1.75	7.44	24.92	–	0.29	0.03	1.00 NiO	–	1250 – 1320	[8]
	55.40	6.00	3.10	2.40	2.30	5.50	25.00	–	0.20	–	–	–	1250 – 1320	[8]
	47.80	–	–	–	14.60	1.90	30.60	5.10	–	–	–	–	1250 – 1300	[9]
	49.10	9.20	3.50	–	5.60	1.90	19.80	8.30	–	2.60	–	–	1150 – 1200	[9]
	44.26	9.06	1.30	–	6.51	2.00	32.34	4.00	–	0.53	0.10	–	1250 – 1300	[9]
	49.17	9.61	3.26	–	6.15	1.90	20.90	9.03	–	–	–	–	1250 – 1300	[9]
Titanium	51.50	10.50	10.50	–	2.50	–	–	–	–	5.50	19.50	–	950 – 1000	[10]
	48.93	9.96	9.96	–	7.38	–	–	–	–	5.24	18.53	–	950 – 1000	[10]
	53.74	–	–	–	2.32	9.91	–	–	–	16.58	17.44	4.53 F	800 – 850	[11]
	44.92	12.28	3.30	1.36	3.74	2.92	11.36	–	–	5.40	14.73	–	980 – 1040	[11]
	50.17	9.32	3.45	1.39	1.84	2.42	10.62	–	–	5.87	14.93	–	980 – 1040	[11]
Zirconium	48.90	12.42	6.55	2.64	1.37	1.45	8.01	–	0.34	–	14.89	3.42 ZrO <sub>2</sub>	950 – 1000	[12]
	43.00	9.40	7.50	4.80	0.20	5.50	2.20	2.30	0.50	–	19.10	5.50 ZrO <sub>2</sub>	950 – 1000	[13]
	39.50	9.00	7.30	4.50	0.20	5.90	6.90	2.30	0.50	–	17.40	5, 50 ZrO <sub>2</sub>	950 – 1000	[13]
Aventurine	47.10	3.50	0.10	–	4.00	6.00	–	0.70	14.70	–	21.90	–	1000 – 1050	[9]
	61.00	1.98	–	–	–	8.72	–	–	16.75	–	11.70	–	1250 – 1300	[1]
Manganese	52.95	9.54	1.85	1.78	3.06	3.54	10.35	–	–	–	16.93 MnO <sub>2</sub>	–	1250 – 1300	[1]

The pyroxene-type crystals forming in pyroxene glazes as small asterisks 0.5 – 1.0 mm in size are of yellow-green color against the background of dark-green or greenish-black glaze glass. Such glazes were popular in China in the 13th century and were used for household chinaware.

The study in [7] considered in detail the chemical and phase composition of the ancient "Tea dust" glazes and arrived at the conclusion that the chemical composition of these glazes was as follows (mole %): 6.75 – 9.17 ( $\text{RO}_2 : \text{R}_2\text{O}_3$ ), 0.9 – 0.87 ( $\text{CaO} + \text{MgO}$ ), 1.63 – 2.73 ( $\text{CaO} : \text{MgO}$ ), 0.12 – 0.24  $\text{Fe}_2\text{O}_3$ . The main crystalline phases in them are pyroxene-type crystals ( $\text{Ca, Mn, Al, FeSi}_2\text{O}_6$ ). In addition to these, cristobalite, wollastonite, and  $\alpha$ -quartz were identified.

**Willemite crystalline glazes** also belong to the macro-crystalline group, since they can contain large spherulite crystals of willemite  $2\text{ZnO} \cdot \text{SiO}_2$  up to several millimeters or even several centimeters in size.

The earliest studies of zinc crystalline glazes were performed in 1847 – 1852. In 1906 Riddle [1] more systematically investigated fritted boron-containing zinc glazes fired at a temperature of 1050 – 1100°C and summarized the effect of the glaze composition on their crystallization. He suggested the following formula of zinc crystalline glaze (wt.%) 27.389 ZnO, 7.382  $\text{KNO}_3$ , 13.770 borax, 7.200 chalk, 4.466 boric acid, 39.693 silicon, 0.6 CuO (above 100%). This corresponds to the following chemical composition of the glaze (%): 2.6535  $\text{Na}_2\text{O}$ , 4.0773  $\text{K}_2\text{O}$ , 4.7839 CaO, 32.4767 ZnO, 47.0662  $\text{SiO}_2$ , 8.9424  $\text{B}_2\text{O}_3$ .

Riddle believed that the coloring additives  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{MnO}$  do not have a significant effect on willemite crystallization, and white willemite crystals keep forming after their introduction, only the background color of the main glaze glass changes.

Norton in 1937 [15] investigated in detail the kinetics of nucleation and crystal growth of zinc glaze with the following molecular formula: 0.0513  $\text{Na}_2\text{O} \cdot 0.2350 \text{K}_2\text{O} \cdot 0.0880 \text{CaO} \cdot 0.5750 \text{ZnO} \cdot 0.0513 \text{BaO} \cdot 0.1620 \text{Al}_2\text{O}_3 \cdot 1.700 \text{SiO}_2 \cdot 0.2020 \text{TiO}_2$  with an additive of 0.25%  $\text{CoO}$ ; all components except for  $\text{Al}_2\text{O}_3$ , CaO, and  $\text{SiO}_2$  are previously fritted.

Norton in his experiments placed the glazed samples into an electric furnace (the temperature variation in the furnace was  $\pm 2^\circ\text{C}$ ), heated them up to 1270°C with holding for 30 min, and then abruptly cooled the samples to different temperatures with 1 h holding. After that he determined the quantity and the maximum sizes of the four crystal types *a*, *b*, *c*, and *d* that emerged and obtained the temperature curves of the nucleation rate and the crystal growth rate.

According to Norton's opinion, the main crystalline phase *a* is willemite. In order to avoid the formation of opaque glaze surface and obtain large crystals *a* in the form of spherulites, it is necessary to heat the glaze up to a sufficiently high temperature (above the crystal growth temperature), at which most nuclei dissolve, then cool it to the temperature of crystal growth and hold at this temperature.

Norton also believed that the crystal growth temperature affects the shape of the crystal and the introduction of some additives (for example,  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$ ) as a catalyst to the glaze composition can modify the glaze melt local viscosity at the crystal growth temperature. This leads to possible controlled crystallization of willemite.

Due to the limitation of the glaze layer thickness, the crystals can grow only within the plane of the glaze coating. Therefore, Norton paid special attention to the syngony of the forming crystals and believed that only the crystals of the hexagonal syngony can produce spherulite formations of large sizes.

Norton's work [15] laid the foundations for subsequent investigations in this field. His research methods and his chief conclusions are still the theoretical basis for the studies of crystalline glazes. However, due to the absence of modern analysis methods, Norton did not perform a qualitative analysis of the emerging four types of crystals and did not fully substantiate his results; therefore, some of his conclusions are hypothetical.

In recent years interest in willemite glazes increased considerably in many countries [8, 9, 12, 16, 17]. The effect of the glaze composition on willemite crystallization, the structural specifics of willemite spherulites, and glaze firing conditions were thoroughly investigated. China, Germany, and Japan are setting up industrial production of porcelain products coated with these glazes. The willemite glazes belong to the  $\text{SiO}_2 - \text{ZnO} - \text{Al}_2\text{O}_3 - \text{CaO}(\text{MgO}) - \text{K}_2\text{O}(\text{Na}_2\text{O})$  system.

According to the data [2, 8, 12, 16, 18], willemite glazes are fired in steps: first, heating up to the ripening temperature (1250 – 1350°C), then chilling to the crystal growth temperature and holding at this temperature. Firing of the glazes should proceed in an oxidizing atmosphere in a smokeless medium, since in a reducing temperature, zinc oxide evaporates from the glaze, which makes the glaze exterior unattractive.

The authors of [8, 12, 17] performed a microscope analysis of the structure and morphology of willemite spherulites and disproved the opinion of Norton [15] who thought that the formation of large spherulites in the glaze coating was determined by the hexagonal syngony of willemite which is capable of growing only in two directions parallel to the glaze surface. The needle-shaped willemite crystals have a fibrous structure and are arranged as intersecting bunches with respect to each other and can grow in the direction of the *C* axis (along the ceramics surface).

**Titanium and zirconium crystalline glazes** were thoroughly studied by numerous Soviet and Russian scientists [10, 11, 13, 19]. As distinct from zinc glazes, these glazes are usually low-melting, opacified by titanium- or zirconium-containing crystals. The glazes belong to the boron-alumino-silicate system. Their maximum firing temperature is 950 – 1100°C. They are usually used in construction and production of sanitary ware, and household faience and majolica products.

A systematic study of the effect of univalent and bivalent metal oxides on the properties and opacification of titanium crystalline glazes when the  $\text{TiO}_2$  molar content in glazes varied from 3.2 to 17% demonstrated [19] that an increase in the  $\text{TiO}_2$  content produces an increase in the amount of the crystalline phase, which lead to an increased degree of opacification. The main crystalline phase of the white glazes containing less than 8%  $\text{TiO}_2$  is sphene. When the content of  $\text{TiO}_2$  is over 8%, rutile crystallizes along with sphene, and with increasing rutile content, the glaze becomes yellow [19].

Zirconium crystalline glazes are most often white and contain 5 to 7 wt.%  $\text{ZrO}_2$ , which crystallizes as zircon or ruffite.

**Aventurine crystalline glazes** are lead-free or low-lead highly alkaline glazes with minute golden spangles which emerge inside the glaze layer due to the introduction of iron, chromium, uranium etc. oxides [2, 3]. Research into these glazes was started in the 1920s [1]. The aventurine glaze crystals look like isolated thin brilliant golden scales and have a high refractive index. These glazes are only applied to faience.

The iron-aventurine glaze is the main representative of this group. It contains 10 – 30% iron oxide, which emerges on cooling in the form of hematite  $\alpha\text{-Fe}_2\text{O}_3$  shaped as rhombohedra [3, 9]. The color of this glaze ranges from light to dark reddish-brown depending on the iron content. The iron-aventurine glazes have the following chemical composition (wt.%): 61.00  $\text{SiO}_2$ , 1.98  $\text{Al}_2\text{O}_3$ , 16.75  $\text{Fe}_2\text{O}_3$ , 11.70  $\text{B}_2\text{O}_3$ , 8.72  $\text{Na}_2\text{O}$ .

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